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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Gas Generator Propellant

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Notice: This application is as filed and may therefore contain an incomplete specification.

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Gas generator propellant

The invention relates to solid gas generator propellants based on guanidine compounds on suitable carriers.

JP H5-254977 discloses gas generator propellants for airbags based on triaminoguanidine nitrate (TAGN), which may additionally contain oxidizing agents such as alkali-metal and alkaline-earth-metal nitrates, nitrites, chlorates or perchlorates. Molybdenum sulphide may be present as a further component. The advantage of using TAGN instead of the known sodium azides is the nontoxic nature and also the good stability of TAGN, which, in addition, does not form any salts which are sensitive to friction and impact in combination with heavy metals. The burn-up rate of the gas generator propellants should be possible via a variation in the compression pressure during the production of pellets or tablets from the component mixture.

Disadvantages of such gas generator propellants are a still inadequate controllability of the burn-up, the development of toxic gases such as CO and an imperfect formation of slag during burn-up, which results in an increased development of dusts, some of which enter the lungs.

Compared with JP H5-254977, the object of the present invention is to provide improved gas generator propellants whose burn-up behaviour can be systematically adjusted and which form readily retainable slags during burn-up and minimize the production of toxic gases. The gas generator propellants are intended to be thermally stable, readily ignitable, fast-burning, even at low temperature, and satisfactorily storable and to ensure a high gas yield. In addition, said gas generator propellants are intended to make it possible to reduce the size of the generator casing and consequently reduce its weight compared with known generators operated with sodium azide.

According to the invention, these objects are achieved by a gas generator propellant, comprising

(A) at least one carbonate, hydrogen carbonate or nitrate of guanidine, aminoguanidine, diaminoguanidine or triaminoguanidine,

(B) at least one alkali-metal or alkaline-earth-metal nitrate or ammonium nitrate as oxidizing agent, and

(C) at least one carrier substance selected from silicon dioxide, alkali-metal silicates, alkaline-earth-metal silicates or aluminosilicates and/or at least one oxygen-supplying carrier substance selected from iron(III) oxide, cobalt oxides, manganese dioxide and copper(II) oxide, to moderate burn-up and improve slag formation.

Carbonates, hydrogen carbonates or nitrates of guanidine, aminoguanidine, diaminoguanidine or triaminoguanidine (TAGN) or its mixtures can be used as component (A). TAGN is preferably used. TAGN is virtually nontoxic (LD_{50} > 3500 mg/kg rat), nonhygroscopic, sparingly soluble in water, thermally stable, combustible at low temperature and has low sensitivity to impact and friction. The gas yield in the burn-up of TAGN is very high, in which process a large proportion of nitrogen gas is produced. Optionally, the TAGN may be replaced by 1 to 50% by weight of nitroguanidine. The cost of the component (A) can thereby be reduced and a beneficial burn-up behaviour achieved, since nitroguanidine has a lower burn-up rate than TAGN.

Alkali-metal or alkaline-earth-metal nitrates, ammonium nitrate and mixtures thereof can be used as oxidizing agents, component (B). Potassium nitrate is preferably used. Potassium nitrate is nonhygroscopic, nontoxic and makes possible a high gas yield during burn-up and a low burn-up temperature.

In the mixture of (A) and (B), component (A) is present in a quantity of about 20 to 55, preferably about 50 to 55% by weight, and component (B) in a quantity of about 80 to 45, preferably about 50 to 45% by weight. Preferably, component (A) is present

in a quantity of about 50 to 55% by weight and component (B) in a quantity of about 50 to 45% by weight.

Silicon dioxide, alkali-metal silicates, alkaline-earth-metal silicates or aluminosilicates or mixtures thereof can be used as carrier substance, component (C). Examples of these are Aerosil 200 and Aerosil 300, highly disperse silicic acid and kieselgur (diatomaceous earth). Preferred carrier substance is silicic acid having a pH of about 7.

Iron(III) oxide, cobalt oxides, manganese dioxide and copper(II) oxide or mixtures thereof can also be used as component (C). The preferred oxygen-supplying carrier substance is iron(III) oxide.

Relative to the total quantity of the components (A) and (B), component (C) is present in a quantity of about 5 to 45, preferably about 8 to 20% by weight. If iron(III) oxide is used as oxygen-supplying carrier substance (C), it is present in a quantity of about 20 to 40, preferably about 25 to 35% by weight, relative to the total quantity of the components (A) and (B).

Component (C) serves to moderate burn-up, i.e. to adjust the burn-up rate. Simultaneously, the slag or melt formation is improved. The slag formation is absolutely necessary, for example, in the case of an airbag.

An airbag essentially comprises a gas generator casing filled with the gas generator propellant, generally in tablet form, and an initial detonator (squib) for detonating the gas generator propellant, and also a gas bag. Suitable detonators are disclosed, for example, in US-PS 49 31 111. The gas bag, which is initially folded into a small pack, is filled, after the initial detonation, with the gases produced in the burn-up of the gas generator propellant and reaches its full volume in a time period of about 10 - 50 ms. The escape of hot sparks, molten material or solids from the gas generator into the gas bag has to be largely prevented, since it could result in a destruction

of the gas bag or in injury to the vehicle occupants. This is achieved by the slag formation.

The formation of slags simultaneously reduces the production of dust-type components which enter the lungs and which could escape from the gas generator of an airbag. Dust-type particles which enter the lungs have a diameter of about 6 μm or less. The oxygen-supplying carrier substances additionally suppress the formation of toxic gases, such as carbon monoxide, during burn-up.

Optionally, the gas generator propellant may furthermore contain, as component (D), a binder which is soluble in water at room temperature. Preferred binders are cellulose compounds or polymers of one or more polymerizable olefinic unsaturated monomers. Examples of cellulose compounds are cellulose ethers, such as carboxymethylcellulose, methylcellulose ether, in particular methylhydroxyethylcellulose. A methylhydroxyethyl-cellulose which can be used satisfactorily is CULMINAL(R) MHEC 30000 PR supplied by the company Aqualon. Suitable polymers having binding action are polyvinylpyrrolidone, polyvinyl acetate, polyvinyl alcohol and polycarbonates.

Relative to the total quantity of components (A) and (B), component (D) is present in a quantity of about 0.1 to 5, preferably about 1.5 to 2.5% by weight.

The binder (D) serves as desensitizing agent and as processing aid in the production of granular material or tablets from the gas generator propellant. It furthermore serves to reduce the hydrophilic nature of the gas generator propellant and to stabilize it.

The tablets or pellets of the gas generator propellant used in the gas generator can be produced by known methods, for instance by hot press working, extrusion, in rotary compression presses or in tableting machines. The size of the pellets or tablets

depends on the desired burn time in the particular application case.

Working Examples

The calculated quantities of triaminoguanidine nitrate (TAGN), optionally also nitroguanidine, and also potassium nitrate and optionally cellulose ether are dissolved in as little water as possible at 90°C and iron oxide and/or silicon dioxide having a mean particle size of approximately 1 μm is stirred into the solution. After predrying at 60°C and 16 hPa with mechanical agitation, the mixture is comminuted in the still moist state and then, after drying at 60°C, is compressed into tablets having a diameter of 6 mm and a height of 2 mm using a tableting machine.

The tested mixtures are listed in Table I. Mixture 1 does not contain any silicon dioxide and Mixture 5 does not contain any iron(III) oxide. As a comparison mixture, Mixture 6 does not contain either silicon dioxide or iron(III) oxide.

Table I: Composition of the mixtures in percentage by weight

	1	2	3	4	5	6
TAGN	39.1	39.1	39.1	29.1	47.3	53.0
Nitroguanidine	-	-	-	10.0	-	-
KNO_3	30.9	30.9	30.9	30.9	40.7	47.0
Fe_2O_3	30.0	20.0	14.0	14.0	-	-
SiO_2	-	10.0	14.0	14.0	12.0	-
Cellulose ether	-	-	2.0	2.0	-	-

Table II shows an overview of the reaction parameters determined by calculation. A high reaction temperature occurs in Mixture 5 and particularly in Mixture 6.

Table II: Calculated values

O_2 balance	%	+2.13	+1.13	-1.84	-1.57	+0.25	+0.84
Volume	ccm	1000	1000	1000	1000	1000	1000
Charging density	(g/ccm)	0.1	0.1	0.1	0.1	0.1	0.1
Pressure	bar	427	444	470	457	654	810
Temperature	K	1973	2116	2116	2116	2468	2666
Number of moles of the gases used	mol/kg	21.1	22.6	23.9	23.4	27.5	28.8
Heat of explosion	J/g	3369	3092	2998	2913	3852	4566

Table III shows an overview of the reaction products produced during burn-up and their quantities.

Table III: Reaction products at 298 K, freeze-out temperature 1,500 K

Compound (% by wt)	1	2	3	4	5	6
CO_2	3.604	10.086	11.538	13.228	12.408	3.768
H_2O	18.952	18.817	18.828	17.711	22.935	26.692
N_2	27.219	27.219	27.217	26.735	33.383	37.596
CO	0.000	0.134	1.283	1.223	0.000	0.000
H_2	0.000	0.017	0.139	0.109	0.000	0.000
NO	0.001	0.000	0.000	0.000	0.009	0.018
O_2	0.001	0.000	0.000	0.000	0.248	0.826
HCN	0.000	0.000	0.000	0.000	0.000	0.000
NH_3	0.000	0.000	0.003	0.002	0.000	0.000
KOH	0.086	0.000	0.003	0.003	0.053	0.101
K_2CO_3	21.014	0.000	0.000	0.000	0.150	31.997
FeO	-	-	12.597	12.597	-	-
Fe_2O_3	3.726	0.000	0.000	0.000	-	0.000
Fe_3O_4	25.396	19.331	0.000	0.000	-	0.000
K_2SiO_3	-	23.572	23.572	23.572	30.813	-
SiO_2	-	0.820	4.820	4.820	-	-

Table IV shows the test results on the susceptibility to decomposition, stability, slag formation and burn-up behaviour of the various mixtures. Mixtures 1 to 5 exhibited good to very good burn-up behaviour, in particular in relation to a constant, high burn rate. Only inadequate slag formation and inadequate burn-up behaviour was observed for the comparison Mixture 6, which did not contain either silicon dioxide or iron(III) oxide as component (C).

<u>Table IV: Test results</u>

Mixture	1	2	3	4	5	6
Decomposition temperature °C Measurement conditions: Heating rate 2°C/min from 15°C below decomposition temperature	*)	-	207	178	203	-
Stability : Holland test Sample weight : 2.5 g Test temperature: 105°C Test time : 72 h Weight loss (% by weight)	-	-	0.28	0.40	0.13	-
Slag formation	++	++	++	++	++	-
Burn-up behaviour	+	++	++	++	+	-

Note: ++ very good; + good; - inadequate

*) For Mixture 1, other stability tests were performed:

Stability tests on Mixture 1

1. Differential thermal analysis
   Apparatus: HERAEUS - FUS-O-MAT
   Heating rate 10°C/min, initial sample mass 10 mg

Result: KNO_3 conversion: 129/130°C
Start of exothermic reaction: 168°C

2. Differential thermogravimetry
Apparatus: LINSEIS - Simultan DTA/TG
Heating rate 5°C/min, initial sample mass 20 mg
Result: KNO_3 conversion: 127°C
Start of exothermic reaction: 135°C
Deflagration: 158°C

Test burn-up of Mixture 1

A test burn-up of Mixture 1 was carried out in a normal aluminium gas generator casing for a 60 litre airbag, provided with a bore for pressure measurement, in a 60 litre can. The test temperature for Test 1 was -35°C and the propellant charge weight was 51.0 g. The propellant charge was composed of tablets having a diameter of 6 mm and a height of 2 mm.

Figure 1 shows the pressure in the burn-up chamber in units of 10^5 pascals as a function of the time after detonation in milliseconds for Test 1.

The pressure build-up takes place within approximately 1.5 ms and the pressure drop to half the maximum pressure takes place after approximately 27 ms. The maximum pressure is $1.88*10^7$ Pa and is reached after 12.3 ms.

Analysis of the toxic gas components formed in ppm

CO 300 NH_3 > 70 NO_x 60

Test burn-up of Mixture 2

The test burn-up of Mixture 2 was carried out in an aluminium Euro gas generator casing for a 35 litre airbag, provided with a bore for pressure measurement, in a 60 litre can. The test

temperature was -35°C in Test 2 and +20°C in Test 3. The propellant charge weight was 41.0 g in Test 2 and 30.0 g in Test 3. The propellant charge was composed of tablets having a diameter of 6 mm and a height of 2 mm.

Figure 2 shows the pressure in the burn-up chamber in units of 10^5 pascals as a function of the time after the detonation in milliseconds for Test 2.

The pressure build-up takes place within approximately 1.5 ms and the pressure drop to half the maximum pressure takes place after approximately 27 ms. The maximum pressure was $1.45*10^7$ Pa and was reached after 15.7 ms.

Figure 3 shows the pressure in the burn-up chamber in units of 10^5 pascals as a function of the time after the detonation in milliseconds for Test 3.

The pressure build-up takes place within approximately 1.5 ms and the pressure drop to half the maximum pressure takes place after approximately 27 ms. The maximum pressure was $1.33*10^7$ Pa and was reached after 7.5 ms.

The gas generator propellant according to the invention is composed of nontoxic, easily producible and inexpensive components whose processing does not present problems. Their thermal stability results in good storage capability. Despite low burn-up temperature, the ignitability of the mixtures is good. They burn rapidly and provide high gas yield with very low CO and NO components. The mixtures according to the invention are therefore particularly suitable for use as gas generating agents in the various airbag systems, as extinguishing agents or propellants. In addition, the gas generator propellants are readily recyclable.

Claims

1. A gas generator propellant, comprising

(A) at least one carbonate, hydrogen carbonate or nitrate of guanidine, aminoguanidine, diaminoguanidine or triaminoguanidine in a quantity of 20 to 55% by weight,

(B) at least one alkali-metal or alkaline-earth-metal nitrate or ammonium nitrate as oxidizing agent in a quantity of 80 to 45% by weight, and

to moderate burn-up and improve slag formation in a quantity of 5 to 45% by weight, relative to the total quantity of components (A) and (B),

(C1) at least one carrier substance selected from silicon dioxide, alkali-metal silicates, alkaline-earth-metal silicates or aluminosilicates and/or

(C2) at least one oxygen-supplying carrier substance selected from iron(III) oxide, cobalt oxides, manganese dioxide and copper(II) oxide.

2. A gas generator propellant according to Claim 1, wherein component (A) is present in a quantity of 50 to 55% by weight, component (B) in a quantity of 50 to 45% by weight and components (C1) and/or (C2), relative to the total quantity of components (A) and (B), in a quantity of 8 to 20% by weight.

3. A gas generator propellant according to Claim 1 or 2, wherein component (A) is triaminoguanidine nitrate.

4. A gas generator propellant according to any one of Claims 1 to 3, wherein component (B) is potassium nitrate.

5. A gas generator propellant according to any one of Claims 1 to 4, wherein component (C1) is silicon dioxide with a pH of about 7.

6. A gas generator propellant according to any one of Claims 1 to 5, wherein component (A) is composed of 99 to 50% by weight of triaminoguanidine nitrate and 1 to 50% by weight of nitroguanidine, relative to the total quantity of component (A).

7. A gas generator propellant according to any one of Claims 1 to 6, wherein component (C2) is iron(III) oxide.

8. A gas generator propellant according to Claim 7, wherein the iron(III) oxide is present in a quantity of 20 to 40, preferably 25 to 35% by weight, relative to the total quantity of the components (A) and (B).

9. A gas generator propellant according to any one of Claims 1 to 8, additionally comprising (D) a binder which is soluble in water at room temperature.

10. A gas generator propellant according to Claim 9, wherein the binder is a cellulose ether, such as carboxymethyl-cellulose, methylcellulose ether and in particular methyl-hydroxyethylcellulose or a polymer of one or more polymerizable olefinic unsaturated monomers.

11. A gas generator propellant according to Claim 9 or 10, wherein the binder is present in a quantity of 0.1 to 5, preferably 1.5 to 2.5% by weight, relative to the total quantity of the components (A) and (B).

12. Use of the gas generator propellant according to any one of Claims 1 to 11 as gas generating agent in airbags, as extinguishing agent or as propellant.

Gas generator propellant

Abstract

The present invention provides a gas generator propellant, in particular for airbags, which contains (A) at least one carbonate, hydrogen carbonate or nitrate of guanidine, aminoguanidine, diaminoguanidine or triaminoguanidine, (B) at least one alkali-metal or alkaline-earth-metal nitrate or ammonium nitrate as oxidizing agent, and (C) at least one carrier substance selected from silicon dioxide, alkali-metal silicates, alkaline-earth-metal silicates or aluminosilicates and/or at least one oxygen-supplying carrier substance selected from iron(III) oxide, cobalt oxides, manganese dioxide and copper(II) oxide to moderate burn-up and improve slag formation. This gas generator propellant has improved burn-up behaviour and slag formation.

Fig. 1

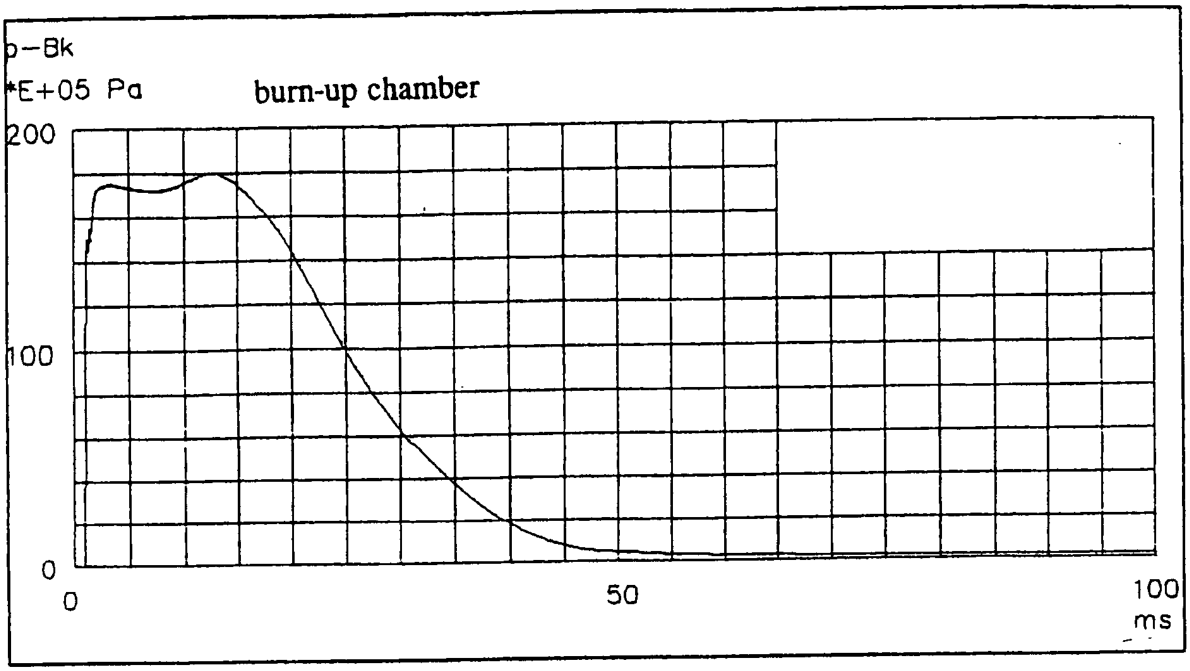
p-Bk
*E+05 Pa
burn-up chamber
200
100
0
0
50
100
ms

Fig. 2

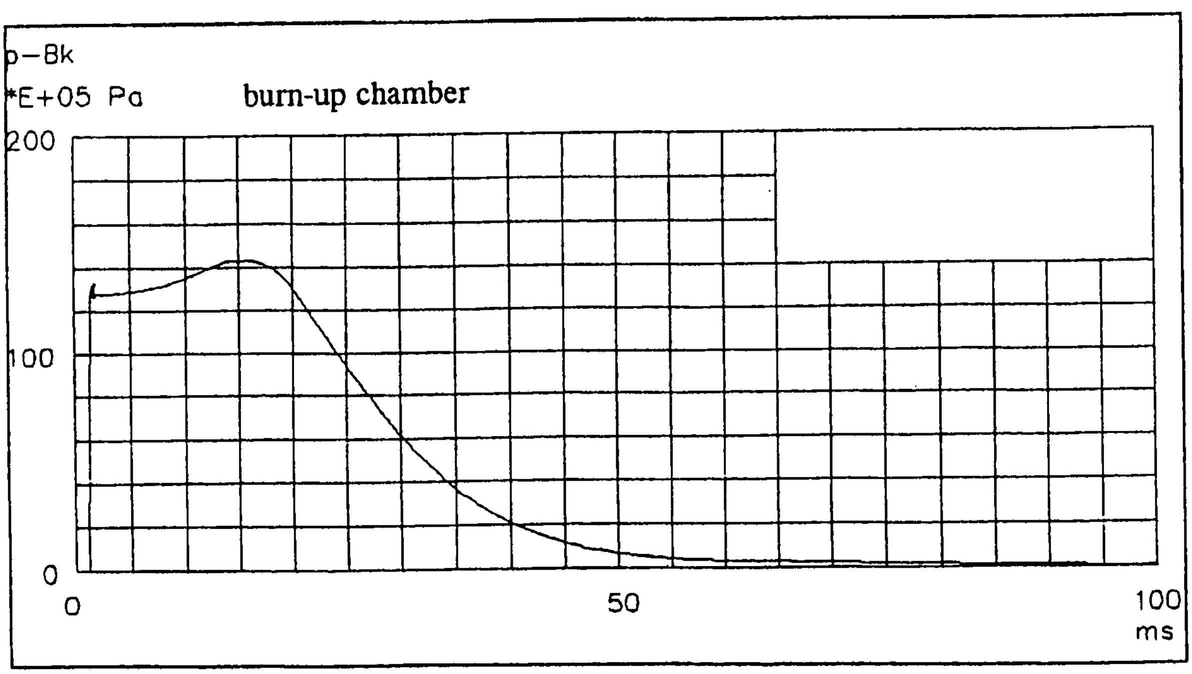
p-Bk
*E+05 Pa
burn-up chamber
200
100
0
0
50
100
ms

Fig. 3